Electronic Supporting Information for:

Dye-Sensitized Photovoltaic Properties of Hydrothermally Prepared TiO_2 Nanotubes

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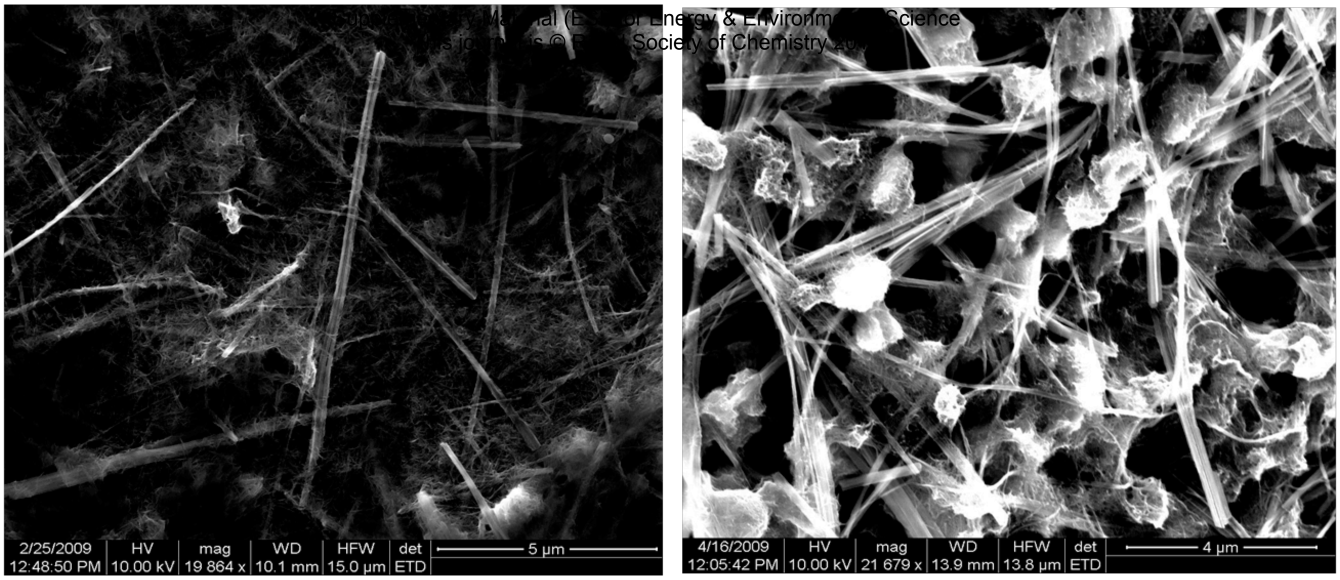


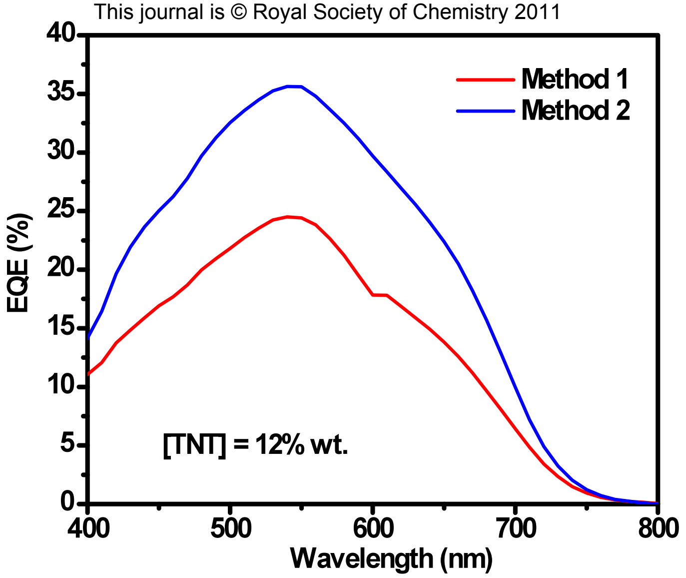
Figure S1. Scanning electron micrographs of the crude reaction mixture of TiO_2 nanotubes immediately after the hydrothermal synthesis. Well-defined nanotubes were observed along with crystallized unreacted NaOH.

Fabrication of TiO_2 nanotube thin films. Since the as-synthesized TiO_2 nanotubes were obtained as a powder material, the fabrication of uniform and mechanically robust films was somewhat challenging. First, the choice of the film-forming component turned out to be very important. In our case, hydroxypropylcellulose (HPC) proved to be the most suitable while the use of poly(ethyleneglycol) (PEG) in the paste recipe resulted in the formation of thin films of very poor quality. Secondly, we also tested two approaches to mix the paste components: 1) manual grinding versus 2) mechanical stirring combined with ultrasonication of the obtained paste. In both cases, TiO_2 nanotubes synthesized at 130 ^{0}C (TNT-130C) were used. Evidently, the latter approach produced TNT films with superior photovoltaic performance. As shown in Figure S2, when the TNT films were made from mechanically stirred and sonicated paste, the device external quantum efficiency (EQE) increased from 24.6 to 36.3%, as measured at λ_{max}. In addition, I-V measurements showed an increase in both open-circuit voltage (V_{OC}), from 0.651 to 0.670 V (or ~ 2.9%), and short-circuit current (J_{SC}), from 5.88 to 6.71 mA/cm^2 (or ~ 14%), that led to the improvement of overall power conversion efficiency (η) by ~ 25%, from 2.24 to

2.81% (Table S1). The rationale for the observed behavior is that thin TiO_2 nanotube films produced via method 2 possessed higher mechanical durability and were more uniform when compared to the films fabricated via method 1. As we noticed, thin films produced after simple manual grinding had a tendency to become damaged upon the device assembly which in turn translated into the loss of the device integrity and, as a result, inferior photovoltaic performance.

Table S1. Average photovoltaic performance parameters of solar cell based on N3-sensitized TNT-130C thin films prepared by 2 different techniques: 1) method 1 – manual grinding of paste components; 2) method 2 – mechanical stirring combined with ultrasonication.

	Area (cm^2)	**EQE_{max} (%)**	**V_{OC} (V)**	**J_{SC} (mA/cm^2)**	**FF (%)**	**η (%)**
Method 1	0.25	24.6	0.651	5.88	58.5	2.24
Method 2	0.25	36.3	0.670	6.71	62.5	2.81



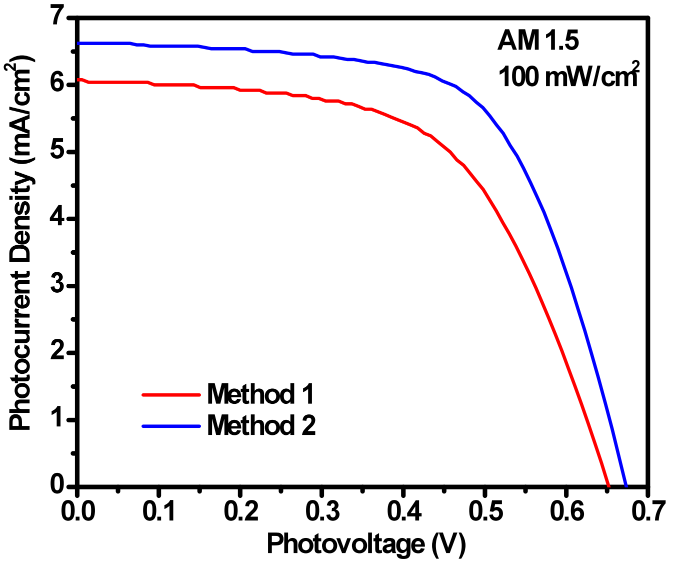


Figure S2. Average photovoltaic performance of solar cell based on N3-sensitized TNT-130C thin films prepared by two different techniques: 1) method 1 – manual grinding of paste components; 2) method 2 – mechanical stirring combined with ultrasonication. Upper – external quantum efficiency (EQE) spectra; lower – current-voltage (I-V) curves. TNT films were sintered at 550 ^{0}C.

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In addition, it is important to emphasize that TiO_2 nanotubes remained intact after being exposed to ultrasonication (Figure S3).

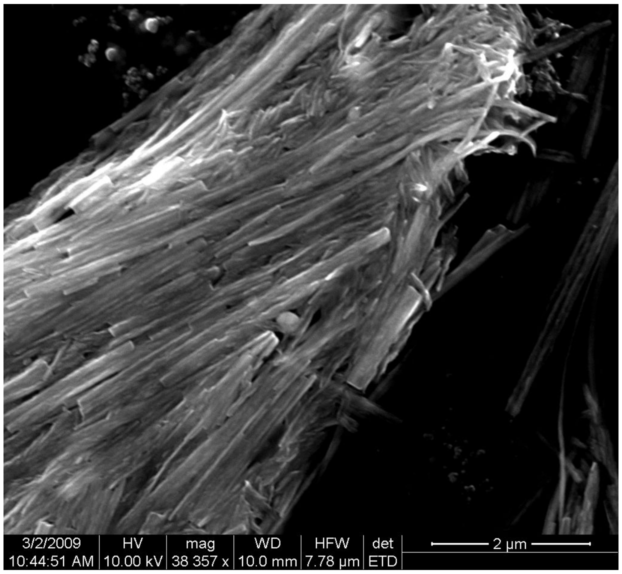


Figure S3. Scanning electron micrograph of TiO_2 nanotubes (TNT-130C) after ultrasonication.

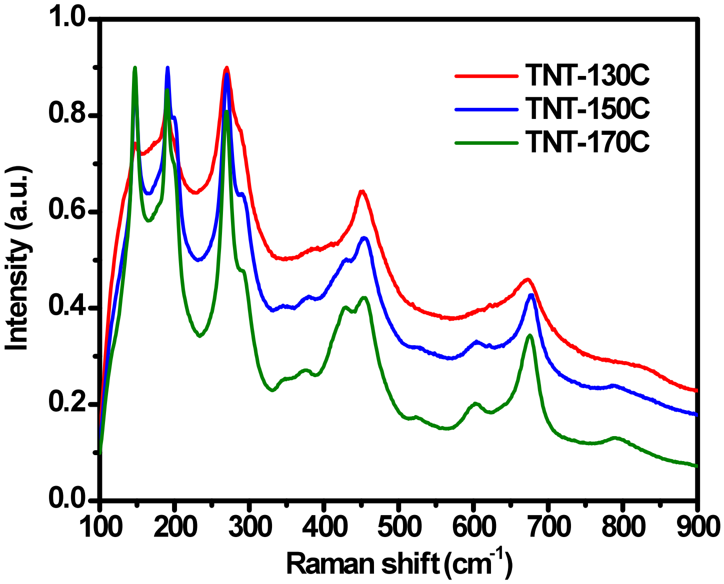
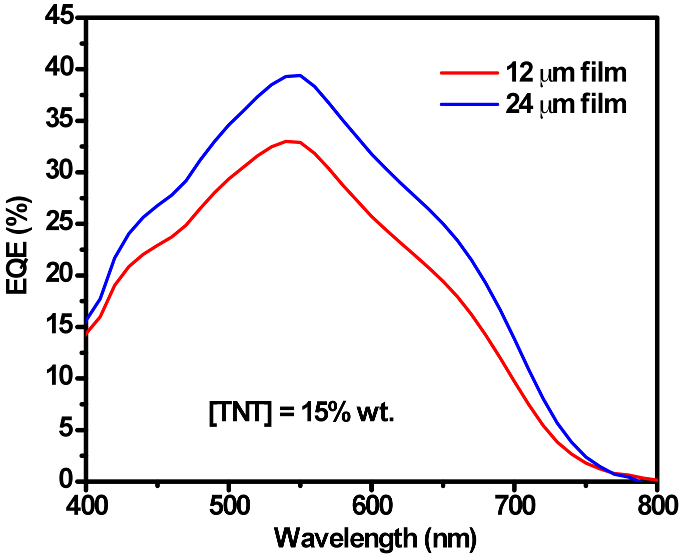


Figure S4. Raman spectra of TiO_2 nanotubes synthesized at different temperatures.

Optimization of TiO_2 nanotube film thickness. In general, the thickness of the resulting TiO_2 film is controlled by two parameters: 1) thickness of a spacer used to doctor-blade the TiO_2 paste, and 2) viscosity of the TiO_2 paste. Since adjusting the paste viscosity could be quite complicated and would require a careful manipulation of the paste composition, we initially optimized the thickness of TiO_2 nanotube film by optimizing the spacer thickness. Scotch tape (Scotch Magic Tape 3M) was used as a spacer and provided an easy way of adjusting the film thickness by simply varying the number of applied tape layers, e.g., from 2 to 4. TiO_2 paste was prepared with TNT content set at 15% wt.

Since the overall film thickness increased from ~ 12 μm for a 2-layer tape to ~ 24 μm for a 4-layer tape, one would expect the deterioration of the overall device photovoltaic response due to the build-up of the internal film resistance. However, this effect was largely overcome by the enhancement of the overall light harvesting efficiency (LHE) due to a nearly 2-fold increase in the concentration of the bound sensitizer molecules. As shown in Figure S5, increasing the number of scotch tape layers from 2 to 4 resulted in the improvement of external quantum efficiency (EQE) from 33.0 to 39.4%, as measured at λ_{max}. The analysis of I-V curves revealed that doubling the film thickness also increased the photocurrent (J_{SC}) by 21.6% (from 6.58 to 8.00 mA/cm^2) while the open-circuit voltage (V_{OC}) remained nearly the same, 0.654 versus 0.662 V. Consequently, the overall power conversion efficiency (η) was boosted by 16.3%, from 2.58 to 3.00% (Table S2). As a result, 4-layer scotch tape doctor-blading technique was concluded to yield the best results.



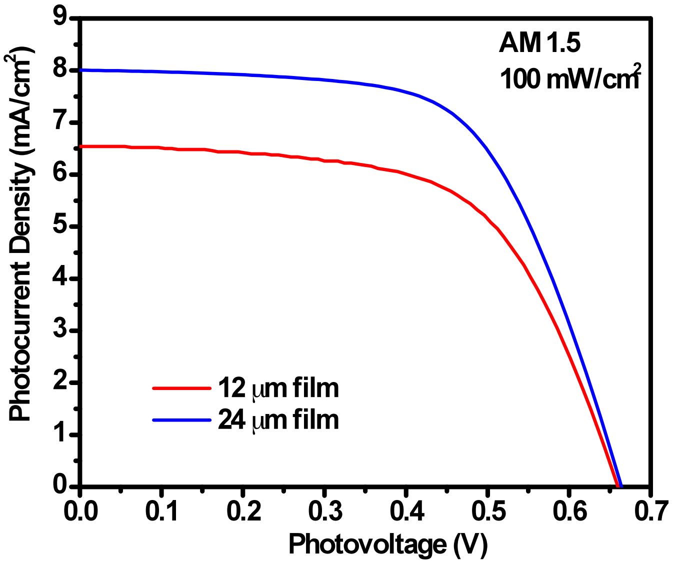


Figure S5. Average photovoltaic performance of N3-sensitized TNT-150C films of different thickness. Upper – external quantum efficiency (EQE) spectra; lower – current-voltage (I-V) curves. TNT content was kept at 15% wt.

Table S2. Average photovoltaic performance parameters of N3-sensitized TNT-150C films of different thickness. TNT content was kept at 15% wt.

Film thickness (μm)	**Area (cm^2)**	**EQE$_{max}$ (%)**	**V$_{OC}$ (V)**	**J$_{SC}$ (mA/cm^2)**	**FF (%)**	**η (%)**
12	0.25	33.0	0.654	6.58	59.8	2.58
24	0.25	39.4	0.662	8.00	58.9	3.00

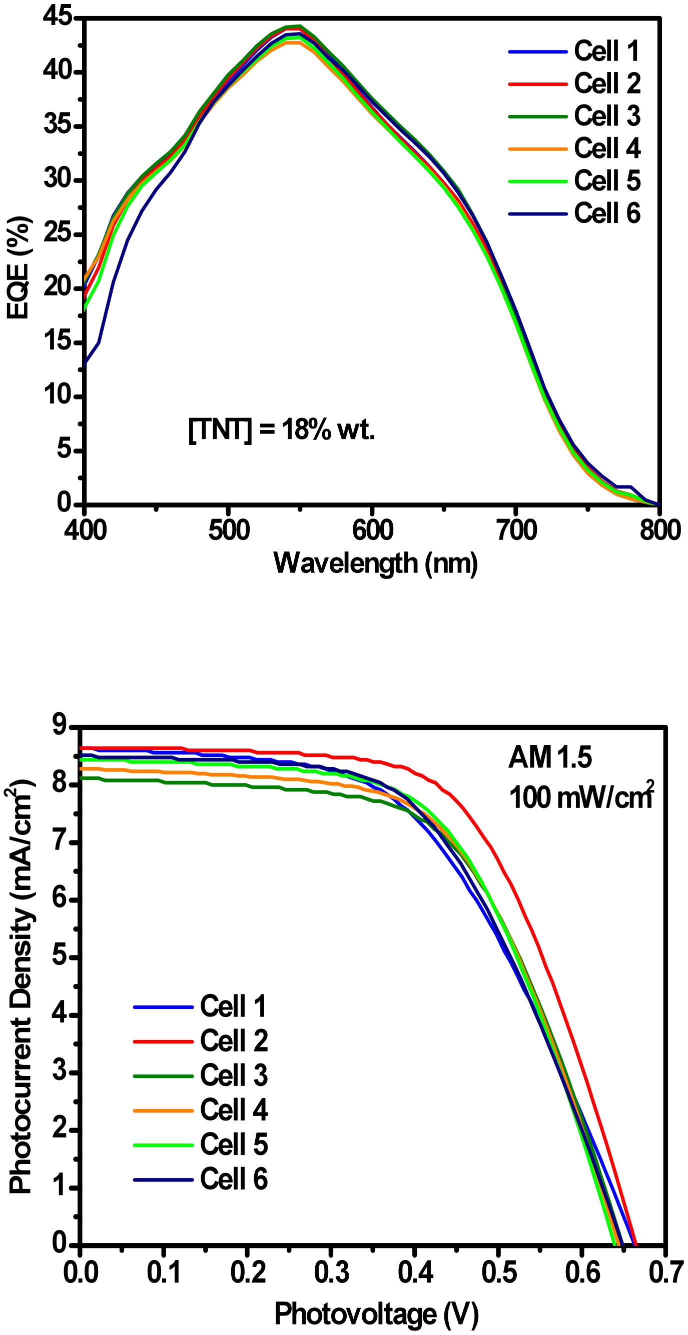


Figure S6. Photovoltaic performance of N3-sensitized TNT-150C solar cells. TNT content was set to 18% wt. Upper – external quantum efficiency (EQE) spectra; lower – current-voltage (I-V) curves.

Table S3. Photovoltaic performance parameters of N3-sensitized TNT-150C solar cells. TNT content was set at 18% wt.

Cell #	Area (cm^2)	EQE_{max} (%)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	η (%)
1	0.25	44.1	0.656	8.74	51.1	2.93
2	0.25	44.0	0.665	8.65	60.4	3.47
3	0.25	44.3	0.649	8.11	58.8	3.09
4	0.25	42.8	0.639	8.44	58.6	3.17
5	0.25	43.2	0.651	7.92	59.5	3.07
6	0.25	43.6	0.649	8.50	55.8	3.08

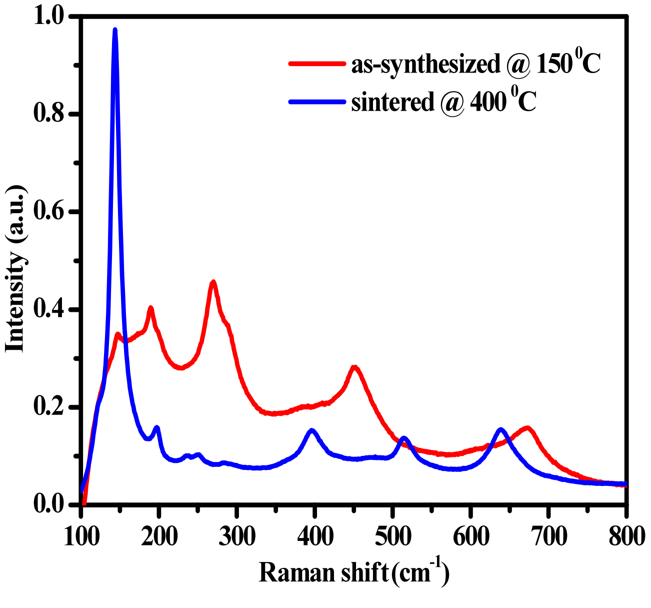


Figure S7. Raman spectra of TiO_2 nanotubes (TNT-150C) after the hydrothermal synthesis (as-synthesized) and after sintering at 400 ^{0}C for 1 hour.

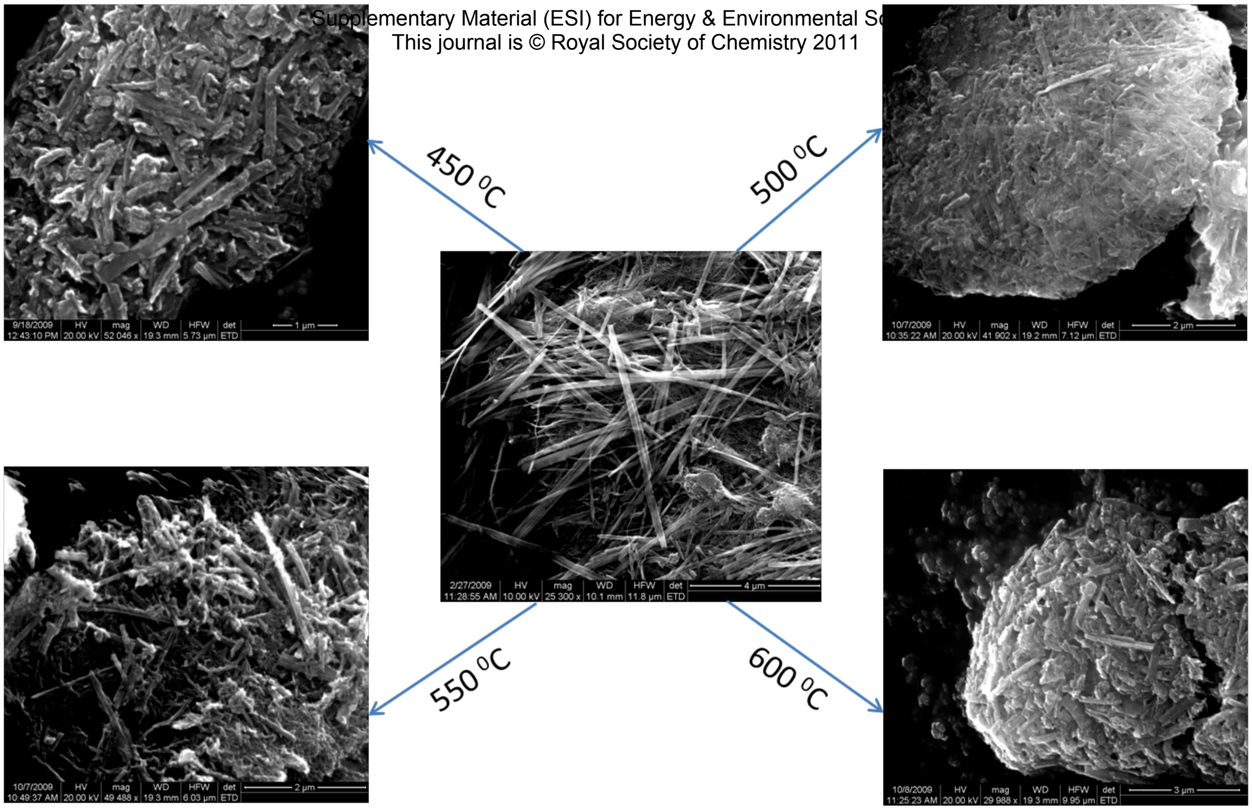
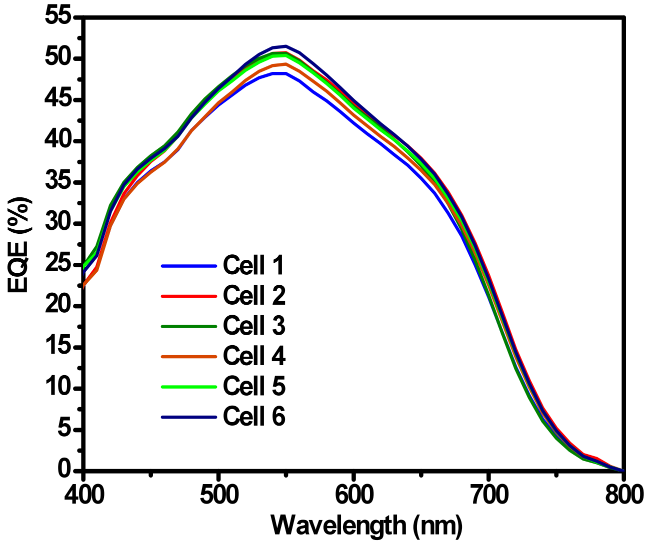


Figure S8. Scanning electron micrographs of N3-sensitized TNT-150C thin films sintered at different temperatures (450-600 ^{0}C).



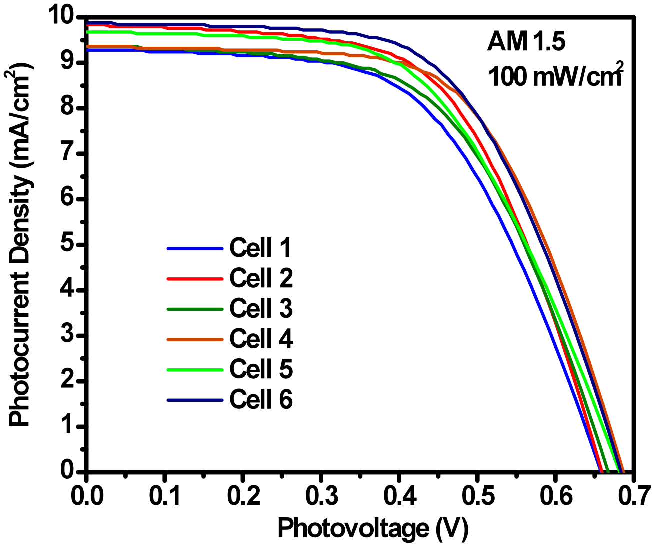


Figure S9. Photovoltaic performance of N3-sensitized TNT-150C solar cells. Nitric acid (HNO_3) was used in paste formulation. TNT content was set to 18% wt. Upper – external quantum efficiency (EQE) spectra; lower – current-voltage (I-V) curves.

Table S4. Photovoltaic performance parameters of N3-sensitized TNT-150C solar cells. Nitric acid (HNO_3) was used in paste formulation. TNT content was set to 18% wt.

Cell #	**Area (cm^2)**	**EQE_{max} (%)**	**V_{OC} (V)**	**J_{SC} (mA/cm^2)**	**FF (%)**	**η (%)**
1	0.25	48.2	0.658	9.29	56.8	3.47
2	0.25	50.7	0.659	9.83	59.0	3.82
3	0.25	50.6	0.667	9.37	57.7	3.61
4	0.25	49.4	0.687	9.36	61.4	3.95
5	0.25	50.4	0.682	9.83	55.2	3.70
6	0.25	51.5	0.684	9.87	59.3	4.00

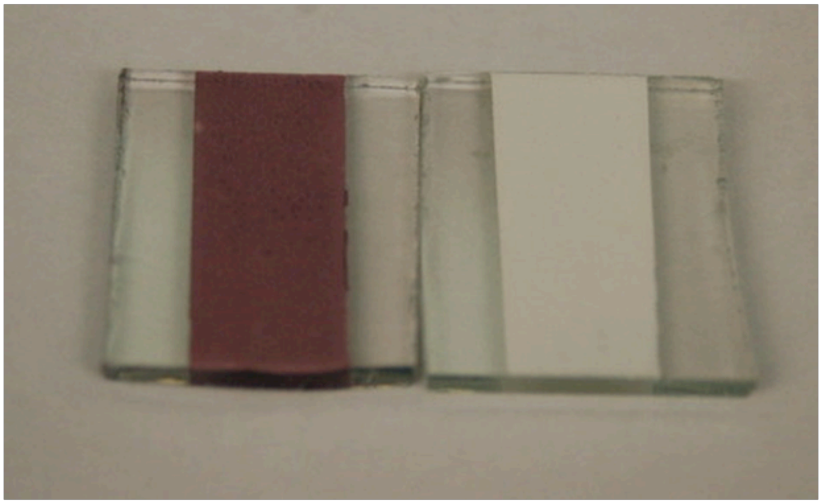


Figure S10. TNT-150C thin films before (right) and after (left) sensitization with N3. Sensitization was carried out at room temperature for 48 hours.